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G03F 7/027**B41C 1/10****B41N 1/06****C08L 35/02****G03F 7/032**(21)Application number : **09-089108**(71)Applicant : **TOYOBO CO LTD**(22)Date of filing : **08.04.1997**(72)Inventor : **KAWAHARA KEIZO****OGI KOJI****IMAI KUMIKO****NISHIMORI NAOKI****KACHI ATSUSHI****IMAHASHI SATOSHI****(54) PHOTSENSITIVE RESIN COMPOSITION, ITS MANUFACTURE, AND PHOTSENSITIVE RESIN USING IT FOR ORIGINAL PRINTING PLATE AND PRINTING PLATE**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide the photosensitive resin material for the printing plate satisfying both requirements of developability in an aqueous solution and resistance to water, especially, a printing ink and superior in workability and storage stability and good in relief reproducibility and superior in elasticity.

SOLUTION: This photosensitive resin composition has a divided phase structure comprising a continuous phase and a fine particle dispersed phase in the continuous phase, and the continuous phase contains an ethylenically unsaturated compound having a number average Mn of ≥ 500 and a weight average molecular weight Mw to Mn ratio of ≥ 2 and a viscosity of ≥ 2000 cP at 20°C, and it is preferred that the dispersed phase comprises core-shell particles each composed of a core phase containing a hydro-phobic polymer and a shell covering the core phase and containing a hydrophilic polymer.

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CLAIMS

[Claim(s)]

[Claim 1] The photopolymer constituent with which it is the photopolymer constituent which has the phase separation structure which consists of a continuous phase and a dispersed phase of the shape of a particle distributed by the continuous phase concerned, and a continuous phase is comparatively characterized by containing the ethylene nature unsaturated compound whose viscosity [in / 2 or more and 20 degrees C / in Mw/Mn] of the weight average molecular weight / as opposed to 500 or more and Mn in number average molecular weight Mn / Mw is 2000 or more centipoises.

[Claim 2] The photopolymer constituent according to claim 1 characterized by being the core-shell particle which a dispersed phase becomes from the shell phase which covers the core phase containing a hydrophobic polymer, and the core phase concerned, and contains hydrophilic polymer.

[Claim 3] The photopolymer constituent according to claim 2 characterized by a continuous phase containing an ethylene nature unsaturated compound according to claim 1 and the hydrophobic polymer which is dissolved with the ethylene nature unsaturated compound concerned unlike the hydrophobic polymer contained in a core phase.

[Claim 4] The manufacture method of a photopolymer constituent that number average molecular weight Mn is characterized by for Mw/Mn mixing the ethylene nature unsaturated compound whose viscosity in 2 or more and 20 degrees C of the weight average molecular weight Mw to 500 or more and Mn is 2000 or more centipoises, hydrophilic polymer, a hydrophobic polymer, the hydrophobic polymer that is dissolved with the ethylene nature unsaturated compound concerned unlike the hydrophobic polymer concerned, and the solvent made to dissolve or swell the hydrophilic polymer concerned, and making a continuous phase and the dispersed phase of a core-shell particle form by phase separation comparatively.

[Claim 5] The original edition for photopolymer printing to which the laminating of a base material and the photosensitive layer containing a photopolymer constituent according to claim 1 to 3 is carried out, and they are characterized by the bird clapper.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the original edition for photopolymer printing and the photopolymer printing version using a photopolymer constituent useful especially as an object for flexographic printing, its manufacture method, and it about the original edition for photopolymer printing and the photopolymer printing version using the photopolymer constituent which can be used for the photosensitive layer of the original edition for photopolymer printing in which development is possible with a drainage system developer, its manufacture method, and it.

[0002]

[Description of the Prior Art] Although what is developed by the organic solvent was known as the photopolymer original edition for the conventional flexographic printing, the problem was in the safety to a human body and environment, such as toxicity and inflammability. Therefore, the original edition for printing in which development is possible is proposed with the drainage system developer as what is replaced with these, for example, it consists of the following photopolymer constituents.

[0003] ** The copolymer which homopolymerizes or copolymerizes and can obtain conjugated-diene system hydrocarbon, alpha, and beta-ethylene nature unsaturated carboxylic acid or its salt, and a monoolefin system unsaturated compound, a photopolymerization nature unsaturation monomer and the photopolymer constituent (JP,52-134655,A --) containing a photosensitizer Refer to JP,53-10648,A and JP,61-22339,A, ** A conjugated-diene system hydrocarbon polymer or the copolymer of a conjugated-diene system hydrocarbon and a monoolefin system unsaturated compound, The photosensitive elastomer constituent which contains a hydrophilic high molecular compound, a non-gas nature ethylene nature unsaturated compound, and a photopolymerization initiator as an indispensable component (refer to JP,60-211451,A), ** There is a photopolymer constituent (refer to JP,60-173055,A) which contains the hydrophobic oligomer and elastomer water bloating tendency matter and photopolymerization initiator which have alpha and beta-ethylene nature unsaturation machine as an indispensable component.

[0004] Moreover, it aims at improvement in performances, such as a mechanical strength of the ** printing version, and impact resilience. It aims at grant of the photopolymer constituent (refer to JP,63-8648,A) containing a hard organic resin particle, and ** water development nature, grant of water-color-ink resistance, and improvement in printing nature. the photopolymer constituent (JP,2-175702,A --) containing a cross-linking resin particle JP,3-228060,A, JP,4-293907,A, JP,4-293909,A, JP,4-294353,A, JP,4-340968,A, JP,5-32743,A, Refer to JP,5-150451,A and JP,5-204139,A, ** It has 2 phase structures for the purpose of the improvement in ink receptiveness of the printing version, a diazo compound and dichromate are included in a continuous phase, and there is a photopolymer constituent (refer to JP,59-36731,B) which contains a particle 10 micrometers or less in a dispersed phase.

[0005]

[Problem(s) to be Solved by the Invention] However, in the original edition for printing using the

photopolymer constituent of above-mentioned **, although the development by the developer of drainage system, for example, alkaline-water solution, and alkaline-water solution-organic-solvent system is possible. The development by the so-called raw practical use water of pH 5.0-9.0 is difficult, and there is a problem that the resistance (henceforth ink-proof nature) over the ink containing the water resistance, water, and/or alcohol of the relief section of the printing version is inadequate. Moreover, if the content of a photopolymerization nature ethylene nature unsaturated compound is made [many] in order to discover the water resistance of the relief section, the cold-flow phenomenon in which the viscosity of the photopolymer constituent before photopolymerization becomes small, and workability falls, and a resin flows out at the time of preservation will arise, and problems -- crosslinking density is too high and rubber elasticity is spoiled -- will produce after photopolymerization.

[0006] In the original edition for printing using the photopolymer constituent of above-mentioned ** or **, in order to enable drainage system development, it is required to contain the hydrophilic component in a continuous phase, and it is necessary to make [many] the content of a hydrophilic component on thermodynamic safety in [content / of a dispersed phase formation component] that case. Therefore, the water resistance (especially ink-proof nature) of the relief section is inferior. If the content of a photopolymerization nature unsaturated compound is made [many] in order to discover the water resistance of the relief section in the above-mentioned case, the cold-flow phenomenon in which the viscosity of the photopolymer constituent before photopolymerization becomes small, and workability falls, and a resin flows out at the time of preservation will arise, and problems -- crosslinking density is too high and rubber elasticity is spoiled -- will produce after photopolymerization. On the other hand, if contents, such as a conjugated-diene system hydrocarbon polymer, are made [many] in order to maintain rubber elasticity, the cold-flow phenomenon in which the viscosity of a photopolymer constituent becomes small like the above, and workability falls, and a resin flows out at the time of preservation will arise.

[0007] In the original edition for printing using the photopolymer constituent of above-mentioned **, it is difficult for the balance of the picture repeatability of the relief section of the printing version, resolution, a degree of hardness, rubber elasticity, a mechanical strength and water development nature, and water resistance (especially ink-proof nature) to be governed by a hard particle size and the hard content of an organic resin particle, and to satisfy each property simultaneously.

[0008] Although it becomes possible in the original edition for printing using the photopolymer constituent of above-mentioned ** to give water development nature by the bridge formation resin particle. Since the hydrophilic component has combined with the bridge formation resin particle, by a resin particle comrade's weld, and condensation. In order that the stable performance cannot be discovered or the distribution state of a particle may change, before photopolymerizing, the viscosity of a photopolymer constituent is changed, and there is a problem that a fall and cold-flow phenomenon of workability arise.

[0009] In the original edition for printing using the photopolymer constituent of above-mentioned **, although it is practical with the thin film versions, such as the lithography version, it is difficult to apply to the thick-film versions, such as a flexographic plate. In order that the performance stabilized by weld of the resin particle comrade in a photopolymer constituent and condensation like above-mentioned ** cannot be discovered or the distribution state of a particle may change also in this case, before photopolymerizing, the viscosity of a photopolymer constituent is changed, and there is a problem that a fall and cold-flow phenomenon of workability arise.

[0010] Although it is required for a photopolymer constituent that compatibility should be good, the rate of light scattering should be low, and a refractive index should be proper. Since the hydrophilic component for enabling above-mentioned drainage system development has high polarity, for the manifestation of coexistence of water development nature and ink-proof nature, and a good sensitization property the kind of hydrophobic component which may fully dissolve when it mixes with this hydrophilic component, and the mixing ratio of a hydrophilic component and a hydrophobic component -- there is a problem to which a rate is limited and to say furthermore, the copolymerization ratio (for example, the copolymerization ratio of the monomer which has a different hydrophilic group, the

copolymerization ratio of the monomer which has a hydrophilic group, and the monomer which has a hydrophobic group) of the monomer which constitutes the polymer which is a hydrophilic component, the copolymerization ratio (for example, copolymerization ratio of the monomer which has a different hydrophobic group) of the monomer which constitutes the polymer which is a hydrophobic component, an usable photopolymerization component, other constituents, and these mixing ratios -- there is a problem that a

[0011] The place which it is made in order that this invention may solve the above-mentioned technical problem, and is made into the purpose does not have condensation of a dispersed phase, it excels in workability and preservation stability, and a conflicting requirement called drainage system development nature and water resistance (especially ink-proof nature) is satisfied, and relief repeatability is good and aims at offering the original edition for photopolymer printing which has the outstanding elasticity, and the photopolymer printing version.

[0012]

[Means for Solving the Problem] By making a continuous phase contain the ethylene nature unsaturated compound which has molecular weight, predetermined molecular weight distribution, and predetermined viscosity, this invention persons find out that the above-mentioned various problems are solved, and came to complete this invention.

[0013] That is, this invention has the following features.

(1) The photopolymer constituent with which it is the photopolymer constituent which has the phase separation structure which consists of a continuous phase and a dispersed phase of the shape of a particle distributed by the continuous phase concerned, and a continuous phase is comparatively characterized by containing the ethylene nature unsaturated compound whose viscosity [in / 2 or more and 20 degrees C / in Mw/Mn] of the weight average molecular weight / as opposed to 500 or more and Mn in number average molecular weight Mn / Mw is 2000 or more centipoises.

(2) The above which is the core-shell particle which a dispersed phase becomes from the shell phase which covers the core phase containing a hydrophobic polymer, and the core phase concerned, and contains hydrophilic polymer Photopolymer constituent of (1).

(3) A continuous phase describes above. The above containing the ethylene nature unsaturated compound of (1), and the hydrophobic polymer which is dissolved with the ethylene nature unsaturated compound concerned unlike the hydrophobic polymer contained in a core phase (2) photopolymer constituents.

(4) The manufacture method of a photopolymer constituent that number average molecular weight Mn is characterized by for Mw/Mn mixing the ethylene nature unsaturated compound whose viscosity in 2 or more and 20 degrees C of the weight average molecular weight Mw to 500 or more and Mn is 2000 or more centipoises, hydrophilic polymer, a hydrophobic polymer, the hydrophobic polymer that is dissolved with the ethylene nature unsaturated compound concerned unlike the hydrophobic polymer concerned, and the solvent made to dissolve or swell the hydrophilic polymer concerned, and making a continuous phase and the dispersed phase of a core-shell particle form by phase separation comparatively.

(5) A base material and the above-mentioned claim (1) - (3) The original edition for photopolymer printing which the laminating of the photosensitive layer containing the photopolymer constituent of a publication is carried out to either, and is characterized by the bird clapper.

(6) Above (5) They are exposure and the photopolymer printing version which subsequently develops negatives and is characterized by the bird clapper about the original edition for photopolymer printing of a publication.

[0014]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The photopolymer constituent of this invention has the phase separation structure which consists of a continuous phase and a dispersed phase of the shape of a particle distributed by the continuous phase concerned. As such phase structure, the following three structures are illustrated, for example.

** Structure from which the hydrophobic polymer became the continuous phase in which hydrophilic

polymer encloses the surroundings of it by the particle-like dispersed phase.

**** Structure where the continuous phase to which a hydrophobic polymer makes a principal component a hydrophobic polymer which the core-shell particle from which hydrophilic polymer became shell with the core is a dispersed phase, and is further different from the hydrophobic polymer concerned encloses the surroundings of a dispersed phase.**

**** Structure from which hydrophilic polymer became the continuous phase in which a hydrophobic polymer encloses the surroundings of it by the particle-like dispersed phase.**

[0015] Hereafter, based on the photopolymer constituent which has the phase structure of ******, this invention is explained in detail. ****** Since the content of a hydrophobic polymer can lessen the content of hydrophilic polymer mostly as for phase structure, although the photosensitive layer using the photopolymer constituent has ink-proof nature, and the shell which consists of hydrophilic polymer of a dispersed phase at the time of development carries out water absorption swelling and it distributes in a developer in this way, water development nature can be discovered, holding ink-proof nature, since the core which consists of a hydrophobic polymer simultaneously was also distributed in the developer.

[0016] ****** The core-shell particle which consists of a shell phase b which the photopolymer constituent which has phase structure covers the continuous phase c containing a hydrophobic polymer, the core phase a containing a hydrophobic polymer, and the core phase concerned, and contains hydrophilic polymer is the photopolymer constituent which was distributed by the continuous phase c and which has phase separation structure.

[0017] in addition, the property to dissolve or swell water or water to the developer contained as a principal component with a hydrophilic property in this invention -- saying -- a hydrophobic property -- water or water -- a principal component -- ****** -- the property in which carry out, and it does not dissolve and swell to the developer to contain is said

[0018] In the photopolymer constituent of this invention, since the shell phase b is formed in the surroundings of the core phase a of adsorption, a meeting, etc. and this core-shell particle does not combine a continuous phase c, a compound which carries out phase separation, without combining the compound of each other [these phases] used for the core phase a, the shell phase b, and a continuous phase c is chosen.

[0019] a. As polymer which forms a core phase in a core phase this invention, in order to make a photopolymer constituent discover ink-proof nature and rubber elasticity, a hydrophobic polymer (henceforth a core phase formation hydrophobic polymer) is used. As such a hydrophobic polymer, the hydrophobic polymer used as a general-purpose elastomer is mentioned, and, specifically, a nonconjugated diene system elastomer and a conjugated-diene system elastomer are mentioned.

[0020] 1) As a nonconjugated diene system elastomer nonconjugated diene system elastomer, the polyolefine system elastomer which has a chlorine atom, and the polyolefine system elastomer which does not have a chlorine atom are mentioned, and these all are used suitably. The elastomer obtained by the polymerization of the monomer which has the elastomer; chlorine atom obtained by chlorinating a polyolefine system elastomer as a polyolefine system elastomer which has a chlorine atom; the elastomer obtained by the reaction of the active substance which has elastomer;, the chlorine, or the chlorine atom obtained by copolymerization of the monomer containing a chlorine atom and the monomer which does not have a chlorine atom, and the polymer which does not have a chlorine atom is mentioned. As an example of a polyolefine system elastomer of having such a chlorine atom for example, a chlorinated polyethylene (ERASUREN by Showa Denko K.K., and the DAISO rack by DAISO Co., Ltd. --) HOLTALIZ by Hoechst A.G., DOW-CPE by the Dow Chemical Co., Chlorination ethylene-propylene rubber (ERASUREN by Showa Denko K.K.), Chlorination isobutylene isoprene rubber, chlorination polypropylene, a vinyl chloride copolymer, a polyvinylidene chloride, An epichlorohydrin rubber, the copolymer of epichlorohydrin and ethylene oxide, the copolymer of epichlorohydrin and a propylene oxide, and the copolymer (the EPIKU roamer by DAISO Co., Ltd. --) of epichlorohydrin and allyl glycidyl ether Good, HYDRIN Made from rich, ZEOSUPAN by Nippon Zeon Co., Ltd., HERCLOR made from Hercules, etc. are illustrated, and a chlorinated polyethylene and a chlorination ethylene propylene rubber are desirable especially. these polymer is independent -- it is --

it is used combining two or more sorts

[0021] When the viscosity of the polyolefine system elastomer which has the above-mentioned chlorine atom takes into consideration the point of phase separation with an ethylene nature unsaturated compound which is mentioned later, as for the Mooney viscosity of a chlorinated polyethylene, it is desirable that it is 10-150 as ML 1+4 (121 degrees C), for example.

[0022] It is 10 - 50 % of the weight more preferably, preferably, five to 60% of the weight, if chlorine content separates from this range, the flexibility will be spoiled, or thermal stability becomes bad, a photopolymer constituent becomes hard or coloring becomes easy to produce the chlorine content of the polyolefine system elastomer which has the above-mentioned chlorine atom.

[0023] As a polyolefine system elastomer which does not have a chlorine atom, ethylene-propylene rubber, isobutylene rubber, an ethylene-propylene-butadiene ternary polymerization object, an acrylic rubber, an ethylene-acrylic rubber, an ethylene vinylacetate copolymer, isobutylene isoprene rubber, iodation isobutylene isoprene rubber, hydrogen-reduction type styrene-polyisoprene rubber, etc. are mentioned. When the viscosity of these polymer takes into consideration the point of phase separation with an ethylene nature unsaturated compound which is mentioned later, as for the Mooney viscosity of ethylene-propylene rubber, it is desirable that it is 20-150 as ML 1+4 (100 degrees C), for example.

[0024] 2) The polymer which is made to carry out the polymerization of the conjugated-diene system hydrocarbon, and is obtained as a conjugated-diene system elastomer conjugated-diene system elastomer, the copolymer which is made to carry out the polymerization of a conjugated-diene system hydrocarbon and the monoolefin system unsaturated compound, and is obtained are mentioned.

[0025] Specifically as the above-mentioned conjugated-diene system hydrocarbon, 1, 3-BUDAJIEN, an isoprene, a chloroprene, etc. are mentioned. these compounds -- independence -- or two or more kinds are combined and it is used

[0026] Specifically as the above-mentioned monoolefin system unsaturated compound, styrene, an alpha methyl styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, acrylonitrile, meta-acrylonitrile, a vinyl chloride, a vinylidene chloride, an acrylamide, a meta-acrylamide, meta-acrylamide vinyl acetate, an acrylic ester, methacrylic-acid ester, etc. are mentioned.

[0027] As the polymer which is made to carry out the polymerization of the above-mentioned conjugated-diene system hydrocarbon, and is obtained, or a copolymer which is made to carry out the polymerization of a conjugated-diene system hydrocarbon and the monoolefin system unsaturated compound, and is obtained Specifically A butadiene polymer, an isoprene polymer, a chloroprene polymer, A styrene-butadiene copolymer, a styrene-isoprene copolymer, a styrene-chloroprene copolymer, An acrylonitrile-butadiene copolymer, an acrylonitrile-isoprene copolymer, An acrylonitrile-chloroprene copolymer, an acrylic-ester-butadiene copolymer, A methacrylic-acid ester-butadiene copolymer, an acrylic-ester-isoprene copolymer, A methacrylic-acid ester-isoprene copolymer, an acrylic-ester-chloroprene copolymer, A methacrylic-acid ester-chloroprene copolymer, acrylonitrile-butadiene-styrene copolymer, an acrylonitrile-isoprene-styrene copolymer, an acrylonitrile-chloroprene-styrene copolymer, etc. are mentioned.

[0028] When the point of phase separation with an ethylene nature unsaturated compound which is mentioned later is taken into consideration about the viscosity of a conjugated-diene system elastomer, it is desirable [the Mooney viscosity of acrylonitrile-butadiene rubber / the Mooney viscosity of 25-95, and a polybutadiene rubber] as ML 1+4 (100 degrees C) that the Mooney viscosity of 25-65, and a polyisoprene rubber is 30-100 as ML 1+4 (100 degrees C) as ML 1+4 (100 degrees C), for example.

[0029] b. The hydrophilic polymer used for a shell phase shell phase is meltable to the developer which contains water or water as a principal component, or polymer (henceforth shell phase formation hydrophilic-property polymer) to swell. Although such hydrophilic polymer is chosen by the kind of a core phase formation hydrophobic polymer or ethylene nature unsaturated compound, and a core phase formation hydrophobic polymer shows higher compatibility, the things (for example, what has the structure where it is common in a molecule, what has a near solubility parameter (SP value), what has near viscosity, the thing said to be affinitive by the rule of thumb) of the structure where the ethylene nature unsaturated compound mentioned later shows low compatibility more are chosen. As such

hydrophilic polymer, it is -COOM1, for example. A machine and -SO three M2 A machine and -CONH2 A machine and -NH2 The polymer which has hydrophilic radicals, such as a machine and -OH basis, is mentioned, and a crosslinked polymer and the chain-like polymer which is not constructing a bridge are also contained.

[0030] the diene system rubber and the maleic anhydride to which copolymerization of general-purpose resins, such as polyvinyl alcohol (PVA) and a carboxymethyl cellulose, an acrylic acid (meta), and the diene compound was specifically carried out -- denaturation -- although liquid polybutadiene, a liquefied polyacrylonitrile-butadiene, etc. are mentioned the bottom -COOM1 A machine or -CONH2 It is desirable to use the hydrophilic polymer which /106 g Has 50-50000Eq of machines. By under /106 g, compatibility [as opposed to water in these bases] is inferior, and 50Eq of ink-proof nature may be inferior, if it may become difficult to develop negatives with neutral water and it exceeds 50000Eq /106 g conversely.

[0031] Above M1 and M2 Either of the ammonium ions which are not replaced [a hydrogen ion, univalent metal ions (for example, Li⁺, Na⁺, K⁺, etc.), divalent metal ions (for example, calcium²⁺ Mg²⁺, etc.), trivalent metal ions (for example, aluminum³⁺ etc.), substitution, or] is said, respectively.

[0032] - COOM1 As Typical Polymer Which Has Machine - COOM1 Polyurethane and -COOM1 Which Have Machine Poly Urea Urethane Which Has Machine, - COOM1 Polyester and -COOM1 Which Have Machine Epoxy Compound Which Has Machine, - COOM1 Polyamide Acid and -COOM1 Which Have Machine Acrylonitrile-Butadiene Copolymer Which Has Machine, - COOM1 Styrene-Butadiene Copolymer and -COOM1 Which Have Machine Polybutadiene Which Has Machine, - COOM1 Polyisoprene and -COOM1 Which Have Machine Polychloroprene Which Has Machine, - COOM1 Although Poly OREFINREN Which Has Machine, Sodium Polyacrylate, Polyacrylamide, Polyvinyl Alcohol (PVA), Carboxymethyl Cellulose (CMC), Hydroxyethyl Celluloses (HEC), These Derivatives, Etc. are Mentioned It is not limited to these.

[0033] Above -COOM1 A machine serves as a gestalt of an acid or a salt. - COOM1 The polymer from which the machine became the gestalt of a salt is obtained by neutralizing the polymer which has -COOH basis. As a compound used in the case of neutralization, a lithium hydroxide, a potassium hydroxide, The hydroxide of alkali metal, such as a sodium hydroxide; A lithium carbonate, potassium carbonate, Carbonic acid alkali-metal salts, such as a sodium carbonate; Potassium-t-butoxide, The alkoxide of alkali metal, such as a sodium methoxide; A calcium hydroxide, Polyvalent metal alkoxides of polyvalent metal, such as a magnesium hydroxide and an aluminum hydroxide, such as hydroxide; aluminum isopropoxide; A triethylamine, TORI Tertiary amine, such as n propylamine; [Diethylamine,] Secondary amine, such as JI n propylamine; Ammonium-salt; magnesium acetates [, such as amino-group content (meta) acrylate; hartshorn salts], such as annular amine;N, such as a morpholine, and N-diethylaminoethyl (meta) acrylate, a calcium acetate, Acetic-acid metal salts, such as an aluminium acetate, etc. are mentioned. These are independent, or they may be used, combining them two or more kinds.

[0034] The above-mentioned hydrophilic polymer may have an ethylene nature unsaturation machine to a molecule end or a molecule inside chain so that you may have a polyoxyalkylene portion further and it may act as a cross linking agent as a hydrophilic radical.

[0035] hydrophilic polymer -- the core phase formation hydrophobic polymer 100 weight section -- receiving -- desirable -- the 3 weight sections - 100 weight section -- 10 weight sections - 70 weight section comes out comparatively more preferably, and it is blended When the water development nature of the photopolymer printing version created from the photopolymer constituent obtained may become inadequate when these loadings are under 3 weight sections and it exceeds the 100 weight sections conversely, water resistance may become inadequate at the photopolymer printing version, and it is not desirable.

[0036] A shell phase may contain other components, as long as it dissolves with the above-mentioned hydrophilic polymer. Hydrophilic polymer, a plasticizer, an elastomer, etc. are mentioned to such a component. [the dissolving ethylene nature unsaturated compound,]

[0037] c. In a continuous-phase this invention, a continuous phase contains a specific ethylene nature

unsaturated compound.

1) The ethylene nature unsaturated compound used by the ethylene nature unsaturated-compound this invention contains at least one ethylene nature unsaturated bond, it carries out chain propagation addition polymerization by the isolation radical, and it has the property which forms a macromolecule polymer. That is, it is the compound in which a photopolymerization reaction is possible, and a polymerization is carried out by UV irradiation etc.

[0038] Comparatively, Mw/Mn is 2-15 preferably two or more, and, as for the ethylene nature unsaturated compound used by this invention, the viscosity in 20 degrees C of the weight average molecular weight (Mw) to Mn whose number average molecular weight (Mn) it is 500-100000 more preferably, and is 500-300000, and a parameter showing molecular weight distribution preferably 500 or more has more preferably 2000 or more centipoises of 2500 or more centipoises of the amounts of macromolecules and hyperviscosity of 3000 or more centipoises.

[0039] Since the ethylene nature unsaturated compounds used by this invention are the amount of macromolecules, and hyperviscosity as described above, a good solid state is maintained before photopolymerization, and work becomes easy, and a cold-flow phenomenon does not generate the photopolymer constituent of this invention at the time of preservation. Moreover, at the time of mixture of each component of a photopolymer constituent, since phase separation of the amount of macromolecules and the hyperviscous ethylene nature unsaturated compound is carried out to the core phase formation hydrophobic polymer which is a solid-state, without dissolving, they can prevent that a core-shell particle carries out condensation weld within a continuous phase. Therefore, the relief repeatability of the photopolymer printing version using such a constituent becomes good.

[0040] Since the molecular weight near [which is a point constructing a bridge] an ethylene nature unsaturation machine is small when Mn of an ethylene nature unsaturated compound is less than 500, near the point constructing a bridge serves as upright structure, and the flexibility of a polymer is spoiled. Moreover, since the distance between the points constructing a bridge becomes small in addition to said reason with [Mw of the compound concerned] 500 [less than] when ethylene nature unsaturation machines are many organic functions, the flexibility of a polymer is spoiled. When Mw/Mn is less than two, the molecular weight distribution near [which is a point constructing a bridge] an ethylene nature unsaturation machine become small, and the flexibility of a polymer is spoiled. Since the prepared photopolymer constituent cannot be solidified good at a room temperature when the viscosity in 20 degrees C is less than 2000 centipoises, work is bad and a cold-flow phenomenon occurs at the time of preservation. In addition, the phase separation of the core phase formation hydrophobic polymer cannot be carried out.

[0041] As such an ethylene nature unsaturated compound, the unsaturation ester of the amount polyols of macromolecules is mentioned. for example, polyethylene-glycol (**) (meta) (urethane) -- acrylate -- polypropylene-glycol (**) (meta) (urethane) -- acrylate -- polytetramethylene glycol (**) (meta) (urethane) -- polyether polyol (**)s (meta) (urethane), such as acrylate, -- acrylate; -- polyols, such as a polyethylene glycol, and a terephthalic acid -- To the polyester polyol obtained by carrying out a condensation reaction, polycarboxylic acids, such as an adipic acid polyester polyol (**) (meta) (urethane) which introduced unsaturation ester -- acrylate; -- polybutadiene polyol (**) (meta) (urethane) -- acrylate -- poly nitril butadiene polyol (**) (meta) (urethane) -- acrylate -- polyisoprene polyol (**) (meta) (urethane) -- acrylate -- polystyrene butadiene polyol (**) (meta) (urethane) -- poly conjugated-diene system polyol (**)s (meta) (urethane), such as acrylate, -- acrylate; -- polyethylene polyol (**) (meta) (urethane) -- acrylate -- polypropylene polyol (**) (meta) (urethane) -- acrylate -- polyethylene propylene polyol (**) (meta) (urethane) -- polyolefine polyol (**)s (meta) (urethane), such as acrylate, -- acrylate; -- although the maleate of the above-mentioned amount polyol of macromolecules etc. is mentioned, it is not limited to this these compounds are independent -- or two or more kinds are combined and it may be used

[0042] The usual esterification methods, such as a direct esterification reaction according [the method of introducing unsaturation ester into the above-mentioned polyol] to the dehydration-ized reaction of a polyol and a unsaturated carboxylic acid and an ester exchange reaction by the dealcoholization reaction

of a polyol and an unsaturation carboxylate, are mentioned. The method of obtaining an ethylene nature unsaturated compound by the dehydration-ized reaction of a polyol, the polymer-ized polyol which is beforehand generated by the dehydration-ized reaction of polyols at the direct esterification reaction by the dehydration-ized reaction of a unsaturated carboxylic acid, and a unsaturated carboxylic acid is also included among these reactions.

[0043] the ethylene nature unsaturated compound used by this invention -- the core phase formation hydrophobic polymer 100 weight section -- receiving -- desirable -- the 10 weight sections - 200 weight section -- the 15 - 150 weight section comes out comparatively more preferably, and it is blended When a core-shell particle carries out condensation weld in the photopolymer constituent obtained when these loadings are under 10 weight sections, and water resistance may be unable to be given to the photopolymer printing version and loadings exceed the 200 weight sections conversely, the water development nature of the original edition for photopolymer printing may become inadequate, and it is not desirable.

[0044] Ethylene nature unsaturated compounds other than the above-mentioned ethylene nature unsaturated compound may be blended, for example, the unsaturation ester of fatty alcohol, such as cetyl alcohol and a stearyl alcohol, etc. is mentioned. In addition, the unsaturation ester of polyols is mentioned. for example, ethylene glycol (**) (meta) -- acrylate and diethylene-glycol (**) (meta) -- acrylate -- glycerol (**) (meta) -- acrylate, 1, and 3-propanediol (**) (meta) -- acrylate -- 1 and 4-butanediol (**) (meta) -- acrylate, 1 and 2, and 4-butane triol (**) (meta) -- acrylate -- 1, 2, 4-butane triol (TORI) (meta) acrylate, 1, and 4-cyclohexane diol (**) (meta) -- acrylate -- 1 and 6-cyclohexane diol (**) (meta) -- acrylate and trimethylol-propane (**) (meta) -- acrylate -- A diallyl phthalate, trimethylol-propane (TORI) (meta) acrylate, diallyl-phthalate, fumaric-acid diethyl, dibutyl-maleate, 1, and 9-nonane diol (**) (meta) -- acrylate, N substitution Male amidation **** (for example, N-MECHIRUMARE amide, N-ECHIRUMARE amide, N-lauryl MAREAMIDO, etc.), etc. are mentioned

[0045] 2) To a hydrophobic polymer continuous phase, it is desirable to contain a hydrophobic polymer in addition to the above-mentioned ethylene nature unsaturated compound at the point of the physical-properties improvement of the constituent after photopolymerization and the improvement in elastic. This hydrophobic polymer is a hydrophobic elastomer, it dissolves with the above-mentioned ethylene nature unsaturated compound, and a core phase formation hydrophobic polymer is a different hydrophobic elastomer. As such a hydrophobic elastomer, conjugated-diene system elastomers (for example, a polybutadiene, acrylonitrile-butadiene rubber, a polyisoprene, a styrene butadiene rubber, a polyisoprene-styrene block copolymer, a polybutadiene-styrene block copolymer, etc.), the polyolefine system elastomer which does not contain chlorine, acrylic rubbers (an ethylene propylene rubber, isobutylene isoprene rubber, etc.), especially ethylene vinyl acetate, etc. are desirable, for example.

[0046] The hydrophobic polymer of a continuous phase is more preferably blended into a constituent at a rate of the 5 weight sections - 120 weight section below the 400 weight sections to the core phase formation hydrophobic polymer 100 weight section. Since the blending ratio of coal of a core phase formation hydrophobic polymer becomes small when these loadings exceed the 400 weight sections, the manifestation of the water development nature of the original edition for photopolymer printing becomes difficult.

[0047] Other components, for example, a photopolymerization initiator, the thermal polymerization inhibitor, the plasticizer, etc. may be blended in addition to the hydrophobic polymer of the above [the photopolymer constituent of this invention], hydrophilic polymer, and the ethylene nature unsaturated compound.

[0048] As a photopolymerization initiator used by this invention, benzophenones and benzoin Acetophenones, benzyls, benzoin alkyl ether, benzyl alkyl ketals, anthraquinone, and thioxan tons are mentioned. specifically A benzophenone, a chloro benzophenone, a benzoin, an acetophenone, A benzyl, a benzoin, a methyl ether, benzoin ethyl ether, Benzoin iso-propyl ether, benzoin isobutyl ether, A benzyl dimethyl ketal, a benzyl diethyl ketal, a benzyl diisopropyl ketal, Anthraquinone, 2-chloro anthraquinone, 2-ethyl anthraquinone, a thioxan ton, 2-chloro thioxan ton, a methyl naphthoquinone, etc. are illustrated, and a benzyl dimethyl ketal, a methyl naphthoquinone, and 2-ethyl anthraquinone are

desirable especially.

[0049] such a photopolymerization initiator -- the constituent 100 weight section -- receiving -- desirable -- 0.01 weight section - 10 weight section -- 0.1 weight sections - 5 weight section comes out comparatively more preferably, and it is blended When there is an inclination which becomes inadequate [photopolymerization start ability] when less than the 0.01 weight section, and 10 weight sections are exceeded, the interior of a photosensitive layer stops hardening by its shading, and there is an inclination for a picture to become easy to be missing [with development].

[0050] It is blended in order to prevent only the polymerization reaction by heat, without suppressing a photopolymerization reaction, and hydroquinone, hydroquinone monomethyl ether, catechol, p-t-butyl catechol, 2, and 6-G t-butyl-p-cresol etc. is mentioned, and a thermal polymerization inhibitor has desirable hadrochinone monomethyl ether, 2, and 6-G t-butyl-p-cresol especially.

[0051] such a thermal polymerization inhibitor -- the constituent 100 weight section -- receiving -- desirable -- 0.01 weight section - 10 weight section -- 0.001 weight sections - 5 weight section comes out comparatively more preferably, and it is blended

[0052] As a plasticizer used for this invention, for example A liquefied polybutadiene rubber, Liquefied polyacrylonitrile butadiene rubber, liquefied polystyrene butadiene rubber, The phthalic ester of the aliphatic hydrocarbon which makes a dioctyl phthalate and diheptylphthalate the start, such as liquid rubber, such as liquefied polyisoprene rubber The trimellitic acid ester which makes trimellitic acid trioctyl the start, Plasticizers, such as adipic-acid system polyester of the 400 to 3000 neighborhood or polyether ester, etc. are mentioned, and plasticizers, such as adipates including adipic-acid 2-ethylhexyl, and molecular weight are independent, or can use together two or more sorts of these.

[0053] When the photopolymer constituent of this invention mixes with a core phase formation hydrophobic polymer, shell phase formation hydrophilic-property polymer, and an ethylene nature unsaturated compound the solvent made to dissolve or swell the hydrophilic polymer concerned, a core phase formation hydrophobic polymer and shell phase formation hydrophilic-property polymer form the dispersed phase which is a core-shell particle by adsorption, a meeting, etc. based on those compatibility, and an ethylene nature unsaturated compound forms a continuous phase. Although such a photopolymer constituent is prepared using the phase separation behavior of each component, the equipment and the method of advancing phase separation are not limited.

[0054] After making the method of mixing or bundling up and mixing each above-mentioned component in arbitrary sequence, and arbitrary solvents swell and distribute each component as an example of the manufacture method of the photopolymer constituent of this invention and making it uniform, the method of removing a solvent is mentioned. Thus, the obtained photopolymer constituent is usually cast by the desired configuration.

[0055] In manufacture of a photopolymer constituent, since the ethylene nature unsaturated compounds which form a continuous phase are the amount of macromolecules, and hyperviscosity, phase separation is carried out to a core phase formation hydrophobic polymer, without dissolving, and a core phase is formed. Although a core phase formation hydrophobic polymer shows higher compatibility, since the ethylene nature unsaturated compound of a continuous phase shows low compatibility more, the shell phase formation hydrophilic-property polymer dissolved or swollen with the solvent covers the surroundings of the core phase which is carrying out phase separation into the continuous phase.

[0056] Moreover, if the hydrophobic polymer to dissolve is further blended with the ethylene nature unsaturated compound concerned unlike a core phase formation hydrophobic polymer, the hydrophobic polymer concerned will dissolve with an ethylene nature unsaturated compound, and will form a continuous phase.

[0057] The photopolymer constituent of this invention is solidified at a room temperature in order to blend the amount of macromolecules, and a hyperviscous ethylene nature unsaturated compound as a continuous phase. For this reason, since the photopolymer constituent of this invention maintains a good solid state before photopolymerization, work becomes easy and a cold-flow phenomenon does not generate it at the time of preservation. The configuration stability expressed with x100% (variation of the thickness of a photosensitive layer : amm) which the photopolymer constituent of this invention

applies 10g of loads on a photosensitive layer with a thickness of 2800mm, and is measured (a/2800) has 2% or less of performance more preferably 5% or less.

[0058] Moreover, since phase separation of the amount of macromolecules and the hyperviscous ethylene nature unsaturated compound is carried out to a core phase formation hydrophobic polymer, without dissolving, it can prevent that a core-shell particle carries out condensation weld within a continuous phase. As for the photopolymer constituent of this invention, the diameter of grain of maximum size of a core-shell particle has 30 micrometers or less of performances of 20 micrometers or less preferably. Therefore, the relief repeatability of the photopolymer printing version using such a constituent becomes good.

[0059] Furthermore, since a dispersed phase is a core-shell particle containing a hydrophobic polymer and it is not necessary to make [many] an ethylene nature unsaturated compound for waterproof grant, it becomes water development nature and compatible [water resistance]. The rate of water swelling expressed with (b-a) when photopolymerizing and making the dry weight ag and this dry into the weight bg after being under 20-degree C ion exchange water for 24 hours / ax100% has 5% or less of performance more preferably 10% or less so that the photopolymer printing version created from the photopolymer constituent of this invention may be mentioned later.

[0060] Since a dispersed phase is a core-shell type particle and it is not necessary to make [many] an ethylene nature unsaturated compound further again for a waterproof manifestation, the degree of cross linking (degree of hardness) of the photopolymer printing version created from the photopolymer constituent of this invention does not become high. The degree of hardness measured by the spring formula hardness test (A type) method according to JIS-K6301 is desirable, 30 to 80 degrees, the rate of impact resilience is desirable and the photopolymer printing version has a performance of 25% or more more preferably 20% or more 30 to 75 degrees. Therefore, the photopolymer printing version which has good elasticity can be obtained.

[0061] ** In the photosensitive layer which has phase structure, although it is desirable that a bridge is not chemically constructed in the state of un-hardening, respectively as for shell phase formation hydrophilic-property polymer and the ethylene nature unsaturated compound of a continuous phase, even if the bridge is constructed over the core phase formation hydrophobic polymer in the state of un-hardening and is not constructed over it, don't care about it. Moreover, even if it is mutually combined chemically after hardening, it is combined with shell phase formation hydrophilic-property polymer and the ethylene nature unsaturated compound of a continuous phase, and it does not matter that there is nothing.

[0062] As long as the manufacturing installation used for mixture of each component is a manufacturing installation which produces the above-mentioned phase separation behavior, what structure is sufficient as it. Although a biaxial extruder, 1 shaft extruder, a pressurized kneader, the Banbury type mixer, or the mixers (for example, ribbon formula stirring wings, support type stirring wings, propeller formula stirring wings, etc.) that have a general stirring function are mentioned as an example of a desirable manufacturing installation, it is not limited to these. As an example of the manufacture method for creating the resin version which mixes each component and becomes by the photopolymer matrix of this invention, although methods, such as the cast method, are held, it is not limited to this.

[0063] The original edition for photopolymer printing of this invention consists of a glue line, a photosensitive layer which consists of an above-mentioned photopolymer constituent, an adhesion prevention layer, and a covering film on a base material preferably. As the manufacture method, a photopolymer constituent is inserted on sandwiches between the base material in which the glue line was formed, and the covering film in which the adhesion prevention layer was formed (carrying out both a glue line and an adhesion prevention layer inside), and the photopolymer version is produced by carrying out heating sticking by pressure. The above-mentioned adhesion prevention layer contains polyvinyl alcohol, a polyacrylamide, a cellulose, a polyamide, etc. As a base material, polyester film, a polyethylene film, a polypropylene film, etc. are used, and polyester film may be used preferably.

[0064] By carrying out UV irradiation of such the original edition for photopolymer printing, the polymerization of the ethylene nature unsaturated compound is carried out, and it is hardened. [at least]

As for especially the ultraviolet rays that irradiate in the case of hardening, what has the wavelength of 300-450nm is desirable 150-500nm, and they are desirable as the light source of such ultraviolet rays, for example. [of a low pressure mercury lamp, a high pressure mercury vapor lamp, the carbon arc light, an ultraviolet-rays fluorescent lamp, a chemical lamp, a xenon lamp, a zirconium lamp, etc.]

[0065] The negative film which has a transparent picture for the above-mentioned original edition for photopolymer printing under the above-mentioned light source is stuck, the photopolymer printing version of this invention irradiates ultraviolet rays, and after carrying out picture exposure, it is obtained by removing the non-picture section for the non-hard spot which is not exposed using an about 20 degrees C - 50 degrees C developer, and forming a relief picture. The photopolymer which is not hardened [by which dissolution removal was carried out] serves as an emulsion or a letter solution of suspension, and remains into a developer tank.

[0066] The surfactant is added at the developer of a drainage system and, as for the developer used, it is important for the above-mentioned hydrophilic polymer to use what is dissolved or distributed for the developer with which this surfactant was added. That is, an usable developer is determined from work safety, the safety to environment, the ease of receiving, etc., and the hydrophilic polymer used for a photosensitive layer according to this is chosen.

[0067] As the above-mentioned surfactant, an anion system surfactant, a cation system surfactant, a Nonion system surfactant, an amphoteric surface active agent, etc. can be used broadly. The addition of a surfactant has 0.01 - 10 desirable % of the weight among a developer. Moreover, you may use the above-mentioned surfactant combining plurality so that optimal development can be performed.

[0068] An operator's safety and the developer of a developer of consideration of environment to a drainage system are desirable, and the organic solvent with which it can mix with water, such as ethanol, an isopropanol, a cellosolve, a glycerol, a polyethylene glycol, a dimethylformamide, a dimethylacetamide, and an acetone, if needed may be mixed.

[0069] To a developer, moreover, sodium carbonate, the Tripoli sodium phosphate, a potassium pyrophosphate, Sodium silicate, sodium sulfate, boric-acid soda, sodium acetate, a magnesium acetate, The neutrality of citric-acid soda, succinic-acid soda, etc., acid or alkaline inorganic or organic salts; A carboxymethyl cellulose, macromolecule system additive [such as a methyl cellulose,]; -- alkali [such as acids, such as a sulfuric acid for pH adjustment, a hydrochloric acid, and a phosphoric acid a sodium hydroxide, a potassium hydroxide, and a calcium hydroxide,]; -- in addition to this, you may add various additives, such as a viscosity controlling agent, a distributed stabilizer, a flocculant, and a zeolite, if needed

[0070] In addition, development is immersed in a developer in the original edition for photopolymer printing, if it is required, it will grind a photopolymer layer against a brush, and it is performed by removing a part for a non-hard spot. The temperature at the time of development has desirable 20-50 degrees C.

[0071] Thus, the obtained photopolymer printing version has rubber elasticity, and is useful as a flexo mark lithographic plate. Moreover, it excels also in ink-proof nature, the transition nature of ink, and ****-proof.

[0072] In addition, the photopolymer constituent of this invention can be applied to the object for FOSHI resists, and sand plastic strikes besides using it as an object for flexo mark lithographic plates, and can be used for the use as an elastomer otherwise hardened by ultraviolet rays, adhesives, a film, a paint, etc. [0073]

[Example] Although the following examples explain this invention concretely, this invention is not limited to these examples. In addition, the section means the weight section among an example. Moreover, relief depth, a degree of hardness, the rate of impact resilience, the rate of water swelling, configuration stability, the existence of core-shell formation, and the existence of particle condensation are shown below.

[0074] 1. measurement condition use device [of Mn of an ethylene nature unsaturated compound, and Mw/Mn]; -- Shimadzu make GPC LC-4A use sample: -- 1-% of the weight THF solution flow rate: -- a part for 1ml/-- column: -- shodexKF-805L measurement temperature: -- 20-degree-CUV wavelength: --

the measuring method rotor formula Brookfield type viscometer of the viscosity of a 220nm². ethylene nature unsaturated compound -- JIS According to K-6726, it measured at 20 degrees C.

3. the relief depth photopolymer printing version -- the difference of the height of the picture section after development, and the non-picture section -- the product made from ONO **** -- it measured by OG-911

4. The rate of 5. impact resilience measured at 20 degrees C about the degree-of-hardness photopolymer printing version with the spring formula hardness test (the A method) according to JIS-K6301 : the height (a) which drops the steel ball of 10mm of diameters (weight of 4.16g) from a height of 20cm, skips, and returns about the photopolymer printing version was read, and $x(a/20)100\%$ was made into indicated value.

6. The rate of water swelling : fabricate a photosensitive-layer resin constituent on the thickness of 0.1cm, 2.0cm long, and a 5.0cm wide sheet, and it is exposure 4000 mJ/cm². It exposed. In 60 degrees C of vacuum dryers, dryness was performed for this sheet for 24 hours. Weighing capacity of this weight was carried out (a (g)). It was under 20-degree C ion exchange water for 24 hours, and weighing capacity of this was carried out to it (b (g)). $(b-a) / a \times 100\%$ were made into indicated value as a rate of water swelling.

7. Configuration stability : the element child of a thickness meter with a cylindrical element child (element child diameter : 10mm and 10g pile of loads) (Ono Sokki DG- 911) was put on the photosensitive-layer side of the base material (total thickness of 2800mm) in which the photosensitive layer which consists of a photopolymer constituent was formed for 60 seconds, the variation (amm) was read, and $x(a/2800)100\%$ was made into indicated value.

8. The core-shell particle and the existence photopolymer constituent of particle condensation were immersed in 1.0% (PURIMO cyanine : Crystal Violet) solution of cation system colors for 30 minutes in 25 degrees C, and hydrophilic polymer was dyed alternatively. It observed whether the core-shell type particle would have produced the state in the matrix with the optical microscope. Furthermore, whether two or more of these core-shell type particles are condensing mutually observed. Two or more core-shell type particles estimated that particle condensation arose, contiguity or when having **-ized.

[0075] It is an amino group to the example 1 <manufacture of hydrophilic polymer I> hexamethylene diisocyanate 276 section, the dimethylol-propionic-acid 145 section, the polyoxy tetramethylene-glycol (product made from PTMG-850:Hodogaya Chemistry) 175 section, the hydroxyethyl methacrylate 60 section, and an end. After dissolving the acrylonitrile-butadiene oligomer (HYCAR-ARBN1300x16:Ube Industries, Ltd. make) 343 section which it has, and the di-n-butyl tin dilaurate 20 section in the tetrahydrofuran 1000 section within a 2l. flask with a cooling pipe, the reaction was performed at 60 degrees C for 4 hours. The end of a reaction was checked by carrying out the fixed quantity of the amount of remains NCO(s). -COOH basis in the formed polymer was neutralized using lithium-hydroxide 1 hydrated salt and magnesium-acetate 4 hydrated salt the half-equivalent every, and hydrophilic polymer I was obtained.

[0076] The liquid polybutadiene (the product made from Idemitsu Petrochemistry-oly-bd R-45HT, number average molecular weight 2800) and the acrylic acid which have a <manufacture of ethylene nature unsaturated compound I> hydroxyl group at the end were mixed, the dehydration-ized reaction was performed, and number average molecular weight 7100 and Mw/Mn obtained the ethylene nature unsaturated compound I whose viscosity in 3.8 or 20 degrees C is 7500 centipoises.

[0077] The <manufacture of photopolymer constituent> above-mentioned hydrophilic-property polymer I The ten sections, the chlorinated-polyethylene (Showa Denko K.K. make : ERASUREN : 301MA; glass transition temperature : -30 degrees C - -25 degrees C) 46 section, The polybutadiene (Japan Synthetic Rubber Co., Ltd. make : BRO2LL, glass transition temperature : -102 degrees C - -75 degrees C) 14 section, The ethylene nature unsaturated compound I The 27 sections, the benzyl dimethyl ketal 1 section, The hydroquinone monomethyl ether 0.1 section, 2, and 6-G t-butyl cresol 0.2 section, the methyl naphthoquinone 0.05 section, the 2-ethyl anthraquinone 0.5 section, the toluene 100 section, and the water 10 section are kneaded with a pressurized kneader at 75 degrees C, and a solvent is removed. The photopolymer constituent was obtained.

Example 2 <manufacture of ethylene nature unsaturated compound II> hydroxyl-group end liquid polybutadiene (the product made from Idemitsu Petrochemistry-oly-bd R45HT, number average molecular weight 2800) and the acrylic acid were mixed, the dehydration-ized reaction was performed, and number average molecular weight 8000 and Mw/Mn obtained the ethylene nature unsaturated compound II whose viscosity in 4.3 or 20 degrees C is 9500 centipoises.

[0078] In the example 1, the photopolymer constituent was obtained by the same method as an example 1 except having used the 27 sections for the ethylene nature unsaturated compound II instead of the ethylene nature unsaturated compound I.

[0079] In example 3 example 1, the photopolymer constituent was obtained by the same method as an example 1 instead of the chlorinated polyethylene except having used the nitril butadiene rubber (Japan Synthetic Rubber Co., Ltd. make : JSR222 SH) 46 section.

[0080] In example 4 example 1, the photopolymer constituent was obtained by the same method as an example 1 except having used the 21 sections, the stearyl metaacrylate 6 section, and the dioctyl-phthalate 10 section for the chlorinated-polyethylene 36 same section as an example 1, the polyisoprene-rubber (Kuraray make : IR- 10) 14 section, and the ethylene nature unsaturated compound I instead of the chlorinated polyethylene, the polybutadiene, and the ethylene nature unsaturated compound I.

[0081] In example 5 example 2, the photopolymer constituent was obtained by the same method as an example 2 instead of the ethylene nature unsaturated compound II except having used the 21 sections, 1, and 9-nonane diol methacrylate 6 section for the ethylene nature unsaturated compound II.

[0082] It is an amino group to the example 6 <manufacture of hydrophilic polymer II> hexamethylene diisocyanate 299 section, the dimethylol-propionic-acid 144 section, the polyoxy tetramethylene-glycol (product made from PTMG-850:Hodogaya Chemistry) 68 section, the hydroxyethyl methacrylate 60 section, and an end. After dissolving the acrylonitrile butadiene oligomer (HYCAR-ARBN1300x16:Ube Industries, Ltd. make) 429 section which it has, and the G N butyl tin dilaurate 20 section in the tetrahydrofuran 1000 section within a 2l. flask with a cooling pipe, the reaction was performed at 60 degrees C for 4 hours. The end of a reaction was checked by carrying out the fixed quantity of the amount of remains NCO(s). Lithium-hydroxide 1 hydrated salt and magnesium-acetate 4 hydrated salt were neutralized for -COOH basis which exists in a reaction solution in half-equivalent [every] solution, and hydrophilic polymer II was obtained.

[0083] The liquid polybutadiene (the product made from Idemitsu Petrochemistry-oly-bd R-45HT, number average molecular weight 2800) and the methyl acrylate which have a <manufacture of ethylene nature unsaturated compound III> hydroxyl group at the end were mixed, the ester exchange reaction was performed, and number average molecular weight (Mn) 5700, Mw/Mn3.1, and the ethylene nature unsaturated compound III whose viscosity in 20 degrees C is 4100 centipoises were obtained.

[0084] In the <manufacture of photopolymer constituent> example 5, the photopolymer constituent was obtained by the same method as an example 5 instead of hydrophilic polymer I and the ethylene nature unsaturated compound II except having used [hydrophilic polymer II] the 21 sections for the ten sections and the ethylene nature unsaturated compound III.

[0085] The polyisoprene (the product made from Idemitsu Petrochemistry-oly-IP) and acrylic acid which have an example 7 <manufacture of ethylene nature unsaturated compound IV> hydroxyl group at the end were mixed, the dehydration-ized reaction was performed, and number average molecular weight (Mn) 8000, Mw/Mn4.0, and the ethylene nature unsaturated compound IV whose viscosity in 20 degrees C is 8000 centipoises were obtained.

[0086] the <manufacture of photopolymer constituent> example 1 -- setting -- instead of [of the ethylene nature unsaturated compound I] -- the ethylene nature unsaturated compound IV -- **** for 27 sections -- things -- except obtained the photopolymer constituent by the same method as an example 1

[0087] In example 8 example 1, the photopolymer constituent was obtained by the same method as an example 1 instead of the ethylene nature unsaturated compound I except having used the acrylate-ized polyisoprene (Kuraray Co., Ltd. make : UCL- 1, number-average-molecular-weight 25000, Mw/Mn= 80000 centipoise viscosity in 3.5 or 20 degrees C) 27 section.

[0088] in example 9 example 1, the photopolymer constituent was obtained by the same method as an

example 1 instead of the ethylene nature unsaturated compound I except having used the oligo butadiene urethane acrylate (: made from Idemitsu Petrochemistry -- 45000 centipoise viscosity in ACR-LC, urethane acrylate [of a hydroxyl-group end polybutadiene (R45HT, number average molecular weight 2800)], number-average-molecular-weight 12000, Mw/Mn=3.5, and 20 degrees C) 27 section [0089] The ethylene nature unsaturated compound V was obtained from making an example 10 <manufacture of ethylene nature unsaturated compound V> polytetramethylene glycol (number average molecular weight 650), isophorone diisocyanate, and hydroxyethyl acrylate react. The number average molecular weight 2000 of the obtained ethylene nature unsaturated compound V, Mw/Mn=3.1, and the viscosity in 20 degrees C were 3000 centipoises.

[0090] the <manufacture of photopolymer constituent> example 1 -- setting -- instead of [of the ethylene nature unsaturated compound I] -- the ethylene nature unsaturated compound I -- the 20 sections and the ethylene nature unsaturated compound V -- **** for 7 sections -- things -- except obtained the photopolymer constituent by the same method as an example 1

[0091] Example 11 <manufacture of ethylene nature unsaturated compound VI> hydroxyl group. Polyol (Mitsubishi Chemical make : polytail HA) 253.7g which carried out hydrogenation of the polybutadiene which it has at the end, hexamethylene diisocyanate 40.8g, and di-n-butyl SUZUJIRA melon rate 2.9g are mixed, and it is N₂. After making it react at 80 degrees C the bottom for 4 hours, hydroxyethyl acrylate 27g and phenothiazin 0.005g were added, the reaction was performed at 80 more degrees C for 4 hours, and the ethylene nature unsaturated compound VI was obtained. The number average molecular weight 9500 of the obtained ethylene nature unsaturated compound VI, Mw/Mn=3.9, and the viscosity in 20 degrees C were 10000 or more centipoises.

the <manufacture of photopolymer constituent> example 5 -- setting -- instead of [of 1 and 9-nonane diol methacrylate] -- the ethylene nature unsaturated compound VI -- **** for 6 sections -- things -- except obtained the photopolymer constituent by the same method as an example 5

[0092] In example 12 example 1, the photopolymer constituent was obtained by the same method as an example 1 instead of the chlorinated polyethylene except having used the styrene styrene-butadiene-rubber block-copolymer (glass transition temperature : -90-degree-C, shell petrochemical company make, Clayton 1101) 46 section.

[0093] Set in the example 13 example 1. The ethylene-propylene-rubber (glass transition temperature : -60 degrees C - -50 degrees-C, JSR-EP51: Japan Synthetic Rubber Co., Ltd. make) 40 section, The isobutylene rubber (glass transition temperature : -75 degrees C - -63 degrees-C, JSR-Butyl 365: Japan Synthetic Rubber Co., Ltd. make) 15 section, The end carboxyl group content butadiene oligomer (HYCAR-CTB2000x162:Ube Industries, Ltd. make) 14 section, The photopolymer constituent was obtained by the same method as an example 1 except having used 25 *****, the same photopolymerization initiator as an example 1, and the thermal polymerization inhibitor for the ethylene nature unsaturated compound I.

[0094] In example 14 example 1, the photopolymer constituent was obtained by the same method as an example 1 instead of the chlorinated polyethylene except having used the acrylic-rubber (Nippon Zeon Co., Ltd. make : NIPOL AR54) 46 section.

[0095] In one to example of comparison 14 examples 1-14, the photopolymer constituent was obtained by the same method as examples 1-14 instead of the ethylene nature unsaturated compound except having used 1 and 6-hexamethylene diacrylate, respectively.

[0096] It evaluated [constituent / photopolymer / which was obtained in examples 1-14 and the examples 1-14 of comparison] about configuration stability, a core-shell particle, the existence of particle condensation, and water bloating tendency. The result is shown in Table 1 or 2.

[0097] Polyester film which has an urethane system glue line with a thickness of 125 micrometers on the <creation of the original edition for photopolymer printing> whole surface, The polyester film which has a polyvinyl alcohol layer with a thickness of 100 micrometers is prepared for the whole surface, the photopolymer constituent which ****ed these polyester film inside and was obtained [polyester film] in the adhesives layer and the polyvinyl alcohol layer in examples 1-14 and the examples 1-14 of comparison is inserted in the shape of sandwiches, and it is 2kg [100 //cm] at 100 degrees C with a heat

press machine. The pressure was put and the sheet with a thickness of 2.9mm was obtained. Next, only the polyester film which has a polyvinyl alcohol layer was exfoliated, it left the polyvinyl alcohol layer on the photopolymer layer, and the original edition for photopolymer printing was obtained.

The negative film which has a picture is stuck on the polyvinyl alcohol layer of the original edition for photopolymer printing <creation of the photopolymer printing version> Obtained, and it is exposure 4000 mJ/cm² at a high intensity lamp (Anderson and hot bulb lamp by the BURI land company). It exposed. After removing a negative film, the neutral water containing 2 % of the weight of alkyl naphthalene sulfonic-acid soda performed development for [40 degrees-C] 15 minutes and with a brush, and the photopolymer printing version was obtained. It evaluated [version / photopolymer printing / which was obtained] about relief depth, the degree of hardness, and the rate of impact resilience. The result is shown in Table 1 or 2.

[0098]

[Table 1]

	リ-7深度 (mm)	硬度	反発弾性率 (%)	水膨潤率 (%)	形状安定性 (%)	アッシュ 形成	粒子凝集
実施例 1	2.0	60	50	2.0	0.5	あり	なし
比較例 1	0.6	70	40	2.1	8.0	あり	あり
実施例 2	1.8	60	50	2.1	0.6	あり	なし
比較例 2	0.7	73	40	2.0	10.0	あり	あり
実施例 3	1.7	61	50	2.0	0.5	あり	なし
比較例 3	0.8	75	40	2.1	9.5	あり	あり
実施例 4	2.0	40	55	2.2	0.6	あり	なし
比較例 4	0.7	75	43	2.0	10.2	あり	あり
実施例 5	1.7	65	45	2.0	0.3	あり	なし
比較例 5	0.6	77	40	2.0	13.4	あり	あり
実施例 6	1.8	60	50	2.3	0.4	あり	なし
比較例 6	0.7	78	35	2.3	12.1	あり	あり
実施例 7	1.8	58	50	2.2	0.5	あり	なし
比較例 7	0.4	75	40	2.4	10.5	あり	あり

[0099]

[Table 2]

	リリーフ深度 (mm)	硬度	反発弾性率 (%)	水膨潤率 (%)	形状安定性 (%)	コアシェル 形成	粒子凝集
実施例 8	1.6	55	55	2.1	0.3	あり	なし
比較例 8	0.6	77	37	2.4	11.5	あり	あり
実施例 9	1.5	65	45	2.0	0.5	あり	なし
比較例 9	0.7	78	40	2.2	11.3	あり	あり
実施例10	1.4	58	45	2.3	0.6	あり	なし
比較例10	0.3	76	37	2.4	10.5	あり	あり
実施例11	1.2	58	40	2.2	0.3	あり	なし
比較例11	0.4	78	40	2.3	10.8	あり	あり
実施例12	2.0	58	55	2.3	0.3	あり	なし
比較例12	0.6	77	40	2.4	10.9	あり	あり
実施例13	1.5	55	45	2.4	0.3	あり	なし
比較例13	0.7	78	35	2.4	11.4	あり	あり
実施例14	1.1	50	40	3.0	0.5	あり	なし
比較例14	0.3	78	30	2.5	10.5	あり	あり

[0100] From Table 1 and Table 2, the photopolymer constituent obtained in the examples 1-14 did not have condensation of a core-shell particle, configuration stability and water bloating tendency were also good, and relief depth is 1.1-2.0mm, and the photopolymer printing version is reproducing the picture of the used negative film faithfully, and has good elasticity, and showed the clear picture also with the sufficient acceptance transition nature of ink.

[0101] However, condensation of a core-shell particle was seen, and configuration stability was also inferior in the photopolymer constituent obtained in the examples 1-14 of comparison, and was in it. Relief depth was 0.3-0.7mm, the photopolymer printing version did not reproduce the picture of the used negative film faithfully, and elasticity was also inferior in it.

[0102]

[Effect of the Invention] According to this invention, there is no condensation of a dispersed phase, it excels in workability and preservation stability, and a conflicting requirement called drainage system development nature and water resistance (especially ink-proof nature) is satisfied, and relief repeatability is good and can offer the original edition for photopolymer printing which has the outstanding elasticity, and the photopolymer printing version so that clearly [in the above explanation].

[Translation done.]